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OXIDATION OF SOLUBLE SULFIDES

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7 Claims

ABSTRACT OF THE DISCLOSURE

A phthalocyanine based catalyst for the oxidation of soluble sulfide compounds is prepared by reacting a soluble metallic phthalocyanine in an alkaline solution with a mercaptan and O₂. A curd-like material comprising a phthalocyanine catalytic complex of increased molecular weight is formed. Such catalytic complex has the unusual property of being soluble in sulfide solution and insoluble in sulfide-free solution. Accordingly, the complex may be used as a homogeneous catalyst for the oxidation of sulfide solutions without excessive catalyst loss in the oxidation zone effluent.

The present invention relates to a method of preparing a phthalocyanine catalytic complex which has unusual solubility characteristics facilitating its use in the oxidation of soluble sulfide compounds. More precisely, the present invention is directed at the resolution of a substantial catalyst recovery problem that has heretofore plagued processes, for the oxidation of soluble sulfide compounds, utilizing a soluble phthalocyanine catalyst. This recovery problem essentially involves the fact that it is desirable, for reasons of reaction rate and of efficient catalyst utilization, to employ a phthalocyanine catalyst that is soluble in the sulfide solution that is to be oxidized, coupled with the fact that the catalyst is too expensive to discard in the treated sulfide solution once its oxidation mission is accomplished. The concept of the present invention stems from my recognition that a phthalocyanine catalyst which is treated with a mercaptan, an alkaline reagent, and oxygen forms a complex which is soluble in an aqueous sulfide solution and insoluble in a substantially sulfide-free, aqueous solution. Accordingly, the present invention essentially involves the use of this remarkable phthalocyanine catalytic complex in the oxygen treatment of sulfide solutions.

As part of the price that has to be paid for a modern industrial society, large quantities of undesired solutions of sulfide compounds are currently available as waste streams from a number of industrial sources. In particular, aqueous solutions containing hydrogen sulfide are undesired side products of many economically significant industrial processes in the chemical, petroleum, and steel industries. For instance, in the petroleum industry, large quantities of solutions of sulfide compounds are produced by such processes as hydrorefining, hydrocracking, reforming, and the like. In fact, a common feature of all these processes is that they operate on a petroleum fraction, a shale oil, a coal tar oil, and the like, which invariably contains organic and inorganic sulfur compounds. During the course of these petroleum processes, these organic sulfur compounds are converted into hydrogen sulfide and hydrocarbons. The resultant hydrogen sulfide is then, typically, removed from these processes by absorption in a suitable scrubbing solution. In a large measure, these scrubbing solutions are aqueous, alkaline solutions, and their disposal presents quite a problem, because of their potential biological oxygen demand which is primarily a consequence of the presence of sul-

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fide ion. In a case of particular interest to the present invention, hydrorefining of petroleum distillates, large quantities of ammonia and hydrogen sulfide are produced, and these are generally absorbed in an aqueous solution which is subsequently withdrawn from the process. In a similar vein, sweetening treatment of a natural gas with a suitable scrubbing fluid, such as monoethanolamine, also results in a solution containing sulfide ions. These solutions are typical of those that are referred to herein as "sulfide solutions," and that constitute the principal input stream to the process of the present invention.

The sulfide compound present in these solutions is generally present as a salt of a strong base such as ammonium sulfide, sodium sulfide, potassium sulfide, and the like, which may be ionized to various degrees. Moreover, the sulfide compound may be present in the same kind of a polar association which characterizes, for instance, solutions of hydrogen sulfide and diethanolamine. In this respect, it should be remembered that hydrogen sulfide because of its polar nature is soluble in an aqueous solution to some degree even in the absence of an appropriate solubility-increasing agent; for example, at 20° C. and 1 atmosphere pressure, 2.5 ml. of hydrogen sulfide will dissolve in one ml. of water. Thus, hydrogen sulfide is within the class of sulfide compounds that are present in these solutions.

Quite understandably, in recent years attention has been focused upon means of converting the sulfide compounds into forms that have less demand for oxygen and, if possible, into a form that has substantial economic value. It has been found, recently, that a particularly preferred process for accomplishing this conversion involves contacting a sulfide solution and oxygen with a phthalocyanine catalyst. Also, it has been found that this process can be utilized, if desired, to transform sulfide compounds into valuable elemental sulfur and, alternatively, into sulfur compounds of reduced oxygen demand suitable for discharge into rivers and streams, if sulfur production is not economically feasible. In addition, it has been determined that this phthalocyanine catalyst may be utilized in combination with a carrier material as a heterogeneous catalyst, or as a sulfide solution-soluble homogeneous catalyst.

From elementary catalysis, it is known to be generally true that the rate of a reaction catalyzed by a heterogeneous catalyst is generally a complex function of the rate of diffusion of the reactants to the surface of the catalyst, the rate of reaction at the surface (this in turn depends directly on the area of exposed catalyst), and the rate of diffusion of the products of the reaction from the catalytic surface. It is equally true that the rate of a reaction catalyzed by a homogeneous catalyst is usually directly proportional to the concentration of the catalyst. Thus, as a general rule, a homogeneous catalyst system is preferable to a heterogeneous catalyst system, because of the vastly increased available catalytic surface area which results in high reaction rates and more efficient utilization of the available catalyst. For this phthalocyanine catalyst, these general rules, indeed, have been found to apply; and the homogeneous system has been found to be, insofar as rate of reaction is concerned, vastly superior to the heterogeneous system. The heterogeneous system, furthermore, has been found to be unusually susceptible to deactivation by elemental sulfur deposition on the surface of the catalyst, while with the homogeneous system this has not been particularly a significant problem. In view of these advantages, it would be expected that the homogeneous system would be the preferred system; however, this has not been the case. The principal reason for this has been the lack of a suitable procedure to recover the homogeneous catalyst once the reaction has been completed, coupled with the prohibitive